The $^{13}C/^{12}C$ of Atmospheric Methane

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INTRODUCTION

For the past 6 years we have been measuring the $^{13}C/^{12}C$ of atmospheric CH_4 on air samples collected at three CMDL sites (BRW, MLO, and SMO) and on the Washington coast at 48°N 126°W.

The $^{13}C/^{12}C$ of atmospheric CH_4 is a tracer that can distinguish between CH_4 input from bacterial and non-bacterial CH_4 sources. Bacterial CH_4 is microbially produced in anoxic environments like swamps, bogs, rice paddies, and the rumens of cows. Non-bacterial CH_4 sources include thermogenically produced natural gas and CH_4 produced during the incomplete oxidation of plant material during biomass burning. Bacterial CH_4 has a $\delta^{13}C$ of about -60‰ (versus PDB) whereas the $\delta^{13}C$ of natural gas and CH_4 produced from biomass burning are about -40 and -27‰, respectively [*Quay et al.*, 1991].

The spatial and temporal variations in the $^{13}C/^{12}C$ of atmospheric CH_4 depend on the variations of the relative strength and $^{13}C/^{12}C$ of the CH_4 sources and sinks. Over interannual time scales the trends in the $^{13}C/^{12}C$ of atmospheric CH_4 indicate changes in the source composition, i.e., the relative strength of bacterial versus non-bacterial CH_4 sources. Because CH_4 will likely contribute about 15% of the radiative forcing during the next century [*Wigley and Raper*, 1992], it is important to quantify the strength of the individual CH_4 sources, currently known to about ±50% and to determine whether the CH_4 source strengths are changing with time. This latter point has been underscored by the recently observed slowdown in the rate of CH_4 increase in the atmosphere [*Dlugokencky et al.*, 1994].

METHODS

The air samples are collected at approximately 2-week intervals, using pre-evacuated stainless steel flasks either 15- or 30-L in volume. The CH_4 is extracted from air in our laboratory using the procedure developed by *Stevens and Rust* [1982]. Briefly, the air is metered into a high-vacuum extraction line through a series of liquid nitrogen traps to remove H_2O, CO_2, and N_2O. The air then passes through a bed of Schutze's reagent, I_2O_5 on silica, to oxidize CO to CO_2 that is trapped cryogenically. Then the CH_4 in the air is combusted over platinized silica at 800°C to CO_2 which is then trapped cryogenically. The yield of the procedure, determined from standards, is 100 ± 2% (n = 114). The $^{13}C/^{12}C$ of the CO_2 derived from CH_4 is measured on a Finnigan MAT 251 gas ratio isotope mass spectrometer. The overall measurement precision is about ±0.1‰. We obtain a $\delta^{13}C$ of -41.73‰ (versus PDB) for NBS-16.

RESULTS AND DISCUSSION

The seasonal cycle in the $\delta^{13}C$ of CH_4 is greatest at 71°N (BRW), with an amplitude of ~0.6‰, and decreases southward to 14°S (SMO) where we measure no significant seasonal trend, i.e. <0.1‰ (Figure 1). The seasonal trends at 71°N and 48°N can be approximated roughly by a single harmonic with an annual period. Episodes of high CH_4 concentrations associated with very depleted $\delta^{13}C$ values occur at these two sites in September-October of each year and are due to input of bacterial methane. Generally, at the northern hemisphere sites the lowest $\delta^{13}C$ values occur in the fall and the highest values occur in the summer. This trend toward higher summertime $\delta^{13}C$ values is expected if CH_4 oxidation by OH primarily controls the seasonal cycle because the $^{12}CH_4$ molecules react at a slightly faster rate (1.0054×) than the $^{13}CH_4$ molecules [*Cantrell et al.*, 1990]. The annual mean $\delta^{13}C$ values increase southward from about -47.8‰ at 71°N to -47.3‰ at 14°S.

We calculate a global average $\delta^{13}C$ of CH_4 of approximately -47.5‰. The mean global $\delta^{13}C$ value, when combined with the ^{14}C content of atmospheric CH_4, yields estimates of the proportion of bacterial, non-bacterial, and fossil CH_4 source strengths [*Quay et al.*, 1991]. We estimate that bacterial CH_4 sources contribute ~70%, fossil CH_4 sources ~20%, and biomass burning ~10% of the total CH_4 input.

Although the seasonal cycle in $\delta^{13}C$ dominates the time-series measurements in the northern hemisphere, there is evidence for a slight interannual increase up until 1992. Measurements at all four time-series locations indicate an increase in $\delta^{13}C$ and, when combined and area weighted, yield an average rate of approximately 0.04 ± 0.02‰ per year. A $\delta^{13}C$ increase indicates the ratio of bacterial to non-bacterial CH_4 source strength is decreasing. In 1993, however, there has been a leveling of the $\delta^{13}C$ trend at the northern sites and a decrease at SMO. This trend is similar to the recent $\delta^{13}C$ decrease observed at Baring Head, New Zealand (41°S) and Scott Base, Antarctica (78°) by *Lowe et al.* [1994], who attribute the decrease to a reduction of the CH_4 released from biomass burning. Measuring the interannual change in the $\delta^{13}C$ of atmospheric CH_4 at several sites over the longer term will be a useful indicator of changes in the proportion of
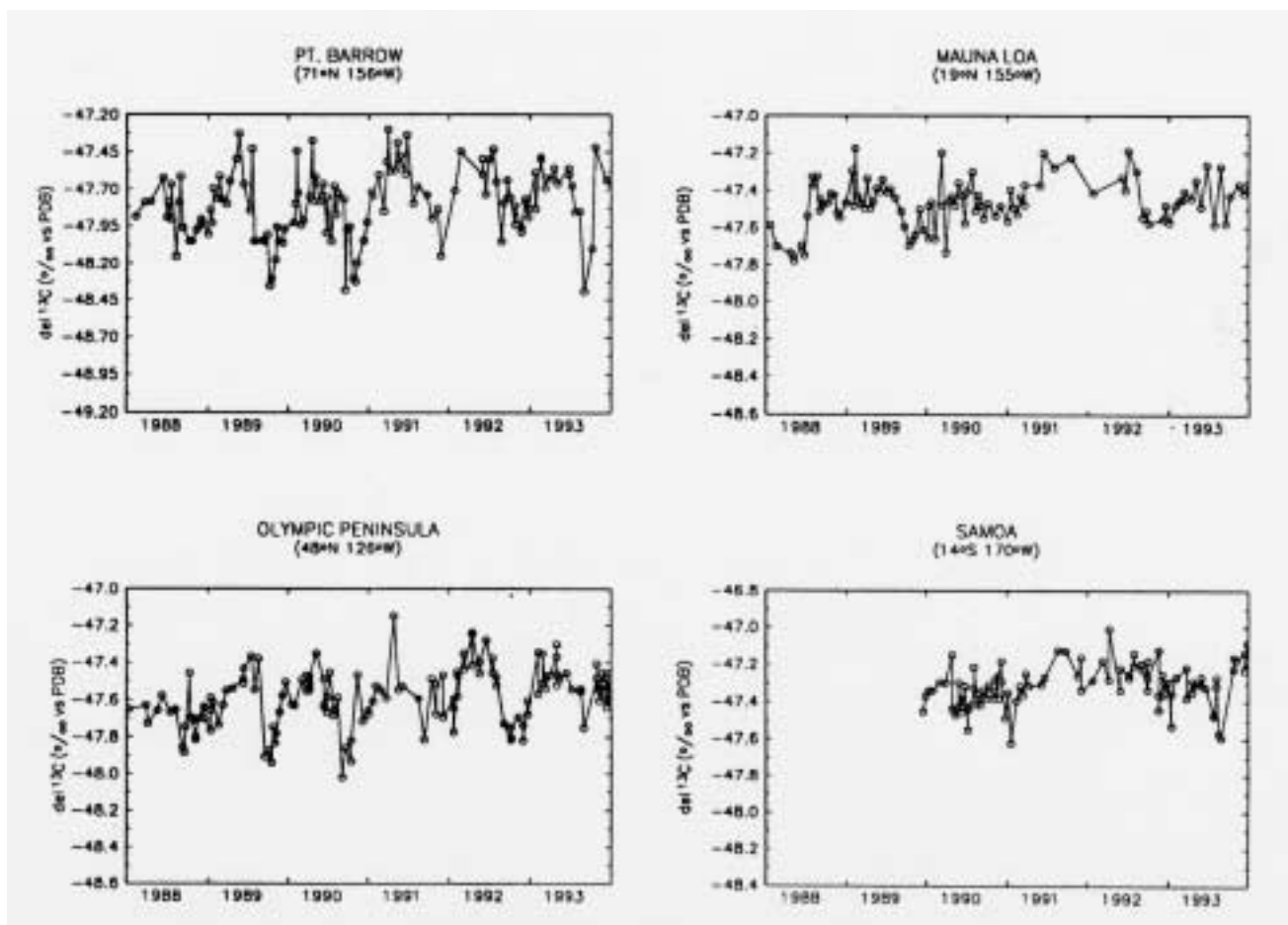
Fig. 1.   The time series of the $\delta^{13}C$ of atmospheric CH_4 measured at BRW, Olympic Peninsula, MLO, and SMO since 1988.

bacterial and nonbacterial CH_4 inputs. These isotopic records should help us determine why the rate of methane increase has slowed so dramatically over the last few years.

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